

Escape-Rate Crossover between Quantum and Classical Regimes in Molecular Magnets: A Diagonalization Approach

Gwang-Hee Kim¹ and E. M. Chudnovsky²

¹*Department of Physics, Sejong University, Seoul 143-747, Republic of Korea*

²*Department of Physics and Astronomy, City University of New York-Lehman College, Bedford
Park Boulevard West, Bronx, New York 10468-1589*

(Received)

Abstract

We have studied numerically the quantum-classical crossover in the escape-rate for an uniaxial spin system with an arbitrarily directed field. Using the simple quantum transition-state theory, we have obtained the boundary separating the first- and the second-order crossover and the escape-rate in the presence of the transverse and longitudinal field. The results apply to the molecular nanomagnet, Mn_{12} .

PACS numbers: 75.45.+j, 75.50.Xx

We consider an easy-axis ferromagnetic nanoparticle, or a molecular cluster, that has metastable or degenerate classical spin states. The direction of the magnetization may change due to two mechanisms. At sufficiently high temperature the rate of the magnetization reversal Γ obeys the Arrhenius law, $\Gamma \sim \exp(-\Delta U/k_B T)$, with ΔU being the height of the energy barrier. At a temperature low enough to ignore the thermal activation, quantum tunneling comes into play with $\Gamma \sim \exp(-\Delta U/\hbar\omega)$ where ω is some temperature-independent frequency related to the shape of the metastable potential well. The crossover between thermal and quantum regimes has been intensively studied in nanospin systems [1–6].

This issue was first raised by Chudnovsky and Garanin, [2] who observed that the crossover in the spin Hamiltonian $\mathcal{H} = -DS_z^2 - H_x S_x$ becomes sharp (first order) for $h_x (\equiv H_x/(2DS)) < 0.25$ and smooth (second order) for $0.25 \leq h_x < 1$. In the exponential approximation, when only the transition exponent is concerned, the first- (second-) order crossover of the escape-rate is characterized by the discontinuity (continuity) of $d\Gamma(T)/dT$ at the crossover temperature, T_0 . Subsequent calculations [4] rendered the boundary between the first- and the second-order crossover for the uniaxial model with a transverse and longitudinal field. It was also pointed out [1,2,4] that the nonanalyticity of the rate for the first-order crossover disappears when quantum corrections to the exponential approximation are computed. The purpose of this Letter is to investigate the “sharpness” of the first-order crossover. This question is especially important in the light of a recent experimental evidence of the first-order crossover in Mn_{12} [9].

We shall focus on the crossover in the molecular magnet Mn_{12} ($S = 10$) [7] when the external magnetic field has both transverse and longitudinal components. In order to calculate the splitting of the excited states, we shall perform a numerical diagonalization of the Hamiltonian. Using numerical results, we then obtain the group of levels which make the dominant contribution to the thermally assisted tunneling. The full problem of the escape rate will be solved by mapping the spin problem onto a particle one [8]. Summing contributions of all excited levels with account of quantum corrections, we will show that

the escape rate becomes analytic for the first-order crossover, but changes sharply around T_0 , in contrast with the second-order crossover. We also obtain the boundary between the two types of the crossover and find that the first-order regime is greatly suppressed by the longitudinal field in accordance with experiment [9].

According to the simple quantum transition-state theory, [10] the escape-rate in the temperature range $T \ll \Delta U$ is given by

$$\Gamma(T) = \frac{1}{Z_0} \sum_m \Gamma_m \exp\left(-\frac{E_m - U_{\min}}{k_B T}\right), \quad (1)$$

where $\Gamma_m = \omega(E_m)W(E_m)/(2\pi)$, $\omega(E_m)$ is the frequency of oscillations at the energy E_m , $W(E_m)$ quantum transition probabilities, and Z_0 the partition function in the well. It is evident from Eq. (1) that the nonanalyticity of the rate is not expected around T_0 for any escape process, even though the crossover can be sharp because of the exponential dependences of Γ_m and thermal populations on the parameters. The rate for the first-order crossover, $\Gamma_I(T)$ is not analytic in the exponential approximation, when the escape rate is approximately given by the dominant term in the summation. However, the summation over all energy levels in Eq. (1) smoothens this non-analyticity.

The model with an arbitrarily directed magnetic field is described by the Hamiltonian

$$\mathcal{H} = -DS_z^2 - H_z S_z - H_x S_x, \quad (2)$$

The zero field Hamiltonian has uniaxial symmetry with easy axis along z and hard plane, xy . H_z is the longitudinal field which affects the height of the energy barrier, and H_x is the transverse field which is responsible for quantum tunneling as well as for the reduction of the barrier. In the first approximation, this spin model describes the magnetic molecule Mn_{12} .

Within the thermally assisted model, the magnetization reversal occurs by quantum tunneling from thermally excited magnetic levels at magnetic fields which bring into resonance the levels m and m' belonging to different potential wells. Denoting m to be the escape level from the metastable well, the resonance condition is that the levels m and m' have the same

energy when $H_z = kD$ where $m' = -m - k$ and k is the bias index. The escape rate from any level is proportional to the product of the probability of the thermal occupation of that level and the probability of quantum tunneling from the level. In this respect, the dominant level for a given temperature is determined by the function [4]

$$f(m) = \frac{\pi(\Delta E_{mm'})^2}{2\omega(E_m)} \exp\left(-\frac{E_m - U_{\min}}{k_B T}\right), \quad (3)$$

where it is assumed that the sum of the linewidths of the m -th and m' -th levels substantially exceeds the level spacing $\omega_{m'} (= E_{m'+1} - E_{m'})$. Here $E_m (= -Dm^2 - H_z m)$ is the energy level of the spin system without transverse field, and $\Delta E_{mm'}$ is the splitting of the pair of in-resonance levels m and m' on the opposite side of the anisotropy barrier. It is seen from Eq. (3) that, since the escape rate decreases exponentially with decreasing temperature, larger longitudinal fields are necessary at lower temperature to produce an observable tunneling rate.

Now, let us calculate the dominant level m_d which maximizes $f(m)$. In order to do that, we first need to find the range of m in the metastable well for a given transverse and longitudinal field, i.e., $-S \leq m \leq m_t \leq 0$, when m_t is the level which is near the top of the barrier and inside the metastable well. For $H_x = 0$ and $H_z = kD$, simple analysis shows that $m_t^0 = -[k/2] - 1$ where $[x]$ gives the integer part of x . Since the height of barrier decreases with increasing H_x , one expects $m_t < m_t^0$. To find the value of m_t we express Eq. (2) in the spherical coordinate and study the energy in the easy plane given by

$$E(\theta, \phi = 0) = -DS^2(\cos^2 \theta + 2h_x \sin \theta + 2h_z \cos \theta), \quad (4)$$

where $h_{x,z} = H_{x,z}/(2DS)$. Writing the height of the barrier as $\Delta U \equiv DS^2(\Delta u)$, m_t is determined by the relation

$$m_t = -\left[\frac{k}{2} + S\sqrt{(1 - h_z)^2 - \Delta u}\right] - 1, \quad (5)$$

where it is noted that, since $\Delta u = (1 - h_z)^2$ in the absence of the transverse field, we obtain $m_t = m_t^0$. Also, $m_t = -S\sqrt{h_x(2 - h_x)}$ at $h_z = 0$. Numerical calculation of Δu of Eq. (4) leads to the results for $m_t(h_x, h_z)$ shown in Fig. 1.

Next, we consider the frequency of the real-time oscillations, $\omega(E_m)$ at the energy E_m . This quantity cannot be calculated with the use of the energy (4) in the spherical coordinate system in which the physical quantity which is equivalent to the mass of the system in a one dimensional case is unknown. Thus, for the mapping of the spin problem onto a particle one, the corresponding energy-dependent frequency is of the form

$$\omega(E) = 2\pi \left(\frac{1}{\sqrt{D}} \int_{x_1(E)}^{x_2(E)} \frac{dx}{\sqrt{E - U(x)}} \right)^{-1} \quad (6)$$

where $x_{1,2}$ are turning points in the particle potential $U(x)$ for a given energy E . Introducing the parameter [2] $p = (U_{\text{sad}} - E_m)/\Delta U$, the specific form of p at a small value of h_x becomes,

$$p = \left(\frac{\frac{m}{S} + h_z}{1 - h_z} \right)^2, \quad (7)$$

where $p = 0$ at the top of the barrier. This gives $m/S = -h_z$, i.e., $m = -k/2$ which is related to m_t discussed previously. After some trivial manipulation of Eq. (6), we obtain the dependence of ω on h_x , h_z , and m . As a result, the frequency of oscillation in $f(m)$ can be numerically deduced by taking $h_x \rightarrow 0$. In this limit the frequency also can be computed for the spin model having the energy levels $E_m = -Dm^2 - H_z m$ as the inversed density of states, i.e., the energy difference between neighboring levels at energy E . This is simply given by $\omega_m \simeq -D(2m + k)$ for $S \gg 1$. Now, in order to calculate the level splitting $\Delta E_{mm'}$, we first consider the formula of the perturbation theory [3]

$$\begin{aligned} \Delta E_{mm'} &= \frac{2DS^{m'-m}}{[(m' - m - 1)!]^2} \\ &\times \left[\frac{(S + m')!(S - m)!}{(S - m')!(S + m)!} \right]^{1/2} h_x^{m'-m}. \end{aligned} \quad (8)$$

This formula is compared with the results from the direct numerical diagonalization. As is illustrated in Table I, there is a disagreement between them for levels with $m \lesssim -6$. However, noting that $m_t(h_x = 0, h_z = 0.1) = -2$ is shifted to $m_t(h_x = 0.05, h_z = 0.1) = -6$, the level $m = -6$ or -7 is important to study the type of the crossover and the escape-rate around T_0 . Accordingly, we will perform the numerical diagonalization for the level splitting of $f(m)$.

Now, we are in a position to calculate the dominant level m_d which is determined by the maximal value of the function (3) for a given temperature. Within the thermally assisted tunneling model the system tunnels through the levels between the bottom and the top. In this process $m_d(T)$ behaves in two different ways. One way is that m_d changes continuously from $-S$ to m_t , whereas the other way is that it performs some discontinuous jump. We call the former - the second-order crossover and the latter - the first-order crossover. As is shown in Fig. 2, for the resonant field $h_z = 0.1$ we have the first-order crossover for $h_x = 0.05, 0.1$ and the second-order crossover for $h_x = 0.15$. Also, for $h_z = 0.4$ ($H_z \simeq 3.28$ Tesla in Mn_{12}), the abrupt shift occurs at $h_x = 0.04$ and the corresponding dominant level changes by 2 ($m_d = -10$ and $m_d = -8$) in the range of temperature (~ 0.1 K $- \sim 1$ K). Strikingly, this feature is observed in a recent experiment, [9] in which the step positions shift abruptly at low temperature and high magnetic field. Employing these schemes in the whole range of h_z , we obtain the phase boundary for the values of the transverse field, which is shown by the symbols in Fig. 3. In the quasiclassical method, the order of the quantum-classical escape-rate crossover was determined by the sign of the coefficient in the expansion of the imaginary-time action near the top of the barrier [4]. In the perturbation method, the behavior of the result (8) is inserted into the calculation of the dominant level m_d in the metastable well, whose behavior determines the type of the order. Using this method, the first-order crossover is found to be suppressed as compared to the quasiclassical method. This was noticed in Ref. [3]. However, as discussed previously, the corresponding level splitting is not quite correct, especially, near the top of the barrier, in which range the perturbation fails. The correct calculation based on the diagonalization method shows that the first-order regime is even more suppressed as compared to the perturbative results. For example, in the unbiased case, the phase boundary becomes at $h_x = 0.114, 0.139$, and 0.25 for the diagonalization, perturbation, and quasiclassical method, respectively. In Fig. 3, there is no data point beyond $h_z = 0.8$. The reason is that $m_t = -9$ in this region and thereby it is meaningless to ask whether the shift is continuous or discontinuous in this region.

The values of the crossover temperature $T_0^{(c)}$ at the phase boundary between first- and second-order crossover, which have been obtained by the diagonalization method described above, are shown in Fig. 4. Comparing this with two other methods, the result based on the diagonalization method is the smallest in the whole range of the bias field. For example, in the unbiased case, we have $T_0^{(c)}/(DS) = 0.117, 0.124, \text{ and } 0.137$ for the diagonalization, perturbation, and quasiclassical method, respectively.

Now, for the relaxation at resonance we will present the results of numerical calculation for the escape rate, $\Gamma(T)$. As is shown in Fig. 5 (as, e.g., for $h_z = 0.1$), the escape rate in the first-order region ($h_x = 0.05$ or 0.1) changes sharply, as shows the comparison with the escape rate in the second-order one ($h_x = 0.15$ or 0.2). Also, for $h_z = 0.4$ we can clearly distinguish the behavior of the rates in two different regimes, e.g., $h_x = 0.04$ and 0.1 , and its trend continues in the whole range of the bias field. The origin of these behaviors is that, as described above, m_d changes discontinuously around T_0 for the first-order crossover, while it does continuously for the second-order one. In other words, since the rate (1) is sensitive to the change of m , the abrupt jump in the first-order crossover induces sharp increase, e.g., $\Gamma(h_x = 0.05, h_z = 0.1)/\Gamma(h_x = 0.2, h_z = 0.1) \simeq 10^6$ at $T/(DS) \simeq 0.12$, and $\Gamma(h_x = 0.04, h_z = 0.4)/\Gamma(h_x = 0.1, h_z = 0.4) \simeq 10^5$ at $T/(DS) \simeq 0.11$.

For the uniaxial spin model considered in this paper, both type of crossover can be realized in the molecular magnet Mn_{12} , and the situation can be controlled by the longitudinal and transverse field. For Mn_{12} , $D \simeq 0.55\text{K}$, and $\Delta U = DS^2 \simeq 55\text{K}$ at $h_x = h_z = 0$ [11,12]. The critical field in the x - or z -direction is $H_{xc} = H_{zc} = 2DS/(g\mu_B) \simeq 8.2\text{T}$, and the longitudinal field for the resonance is $H_0 = D/(g\mu_B) \simeq 0.41\text{T}$. At these fields, the magnetic relaxation in Mn_{12} can occur on measurement time scales, and gives rise to the different behavior of the dominant level and the rate in magnetization depending on H_x and H_z . Furthermore, in the unbiased case the first-order crossover can be observed in the field range $0 < H_x < 0.93$ Tesla and the crossover region occurs at the temperature range $\sim 0.1 \text{ K} < T < \sim 1 \text{ K}$. This field range decreases with increasing the bias field. Even though

we presented the results of m_d only for $h_z = 0.1$ and 0.4 in Fig. 2, we have found that the levels which, at a certain temperature, change by more than 1 are $m = 7, 8$ or 9 depending on the value of the resonant field.

In conclusion, we have studied the quantum-classical crossover of the escape-rate of a uniaxial spin model with an arbitrarily directed field. Employing the diagonalization method, we have obtained the dominant level for the thermally assisted tunneling and dependence of the escape rate on temperature. In comparison to the previously studied models, the first-order region is greatly suppressed, but still observable in molecular magnets. It is also found that the first-order crossover is fairly sharp while the second-order the crossover is smooth. This is found to be strongly related with the discontinuous (continuous) jump of m_d in lower (higher) field h_x . These results have been applied to the high-spin molecule, Mn_{12} . They are also relevant to the study of nanoparticles.

G.-H. K. is grateful to A. Garg for useful discussions. E. C. acknowledges support from the NSF Grant DMR-9978882. G.-H. K. was supported by grant No. 1999-1-114-002-5 from the Interdisciplinary Research Program of the KOSEF.

REFERENCES

- [1] Chudnovsky E. M., Phys. Rev. A **46** (1992) 8011 .
- [2] Chudnovsky E. M. and Garanin D. A., Phys. Rev. Lett. **79** (1997) 4469 .
- [3] Garanin D. A. and Chudnovsky E. M., Phys. Rev. B **56** (1997) 11102.
- [4] Garanin D. A., Martínez Hidalgo X., and Chudnovsky E. M. , Phys. Rev. B **57** (1998) 13639.
- [5] Liang J.-Q., Müller-Kirsten H. J. W., Park D. K., and Zimmerschied F., Phys. Rev. Lett. **81** (1998) 216.
- [6] Kim G.-H., Phys. Rev. B **59** (1999) 11847; *ibid.* **60** (1999) 6262; J. Appl. Phys. **86** (1999) 1062; Choi T. S. and Kim G.-H., **291** (2000) 219.
- [7] Friedman J. R., Sarachik M. P., Tejada J., and Ziolo R., Phys. Rev. Lett. **76** (1996) 3830; Thomas L., Lioni F., Ballou R., Gatteschi D., Sessoli R. and Barbara B., Nature **383** (1996) 145.
- [8] Zaslavskii O. B. and Ul'yanov V. V., Sov. Phys. JETP **60** (1984) 991; Zaslavskii O. B., Phys. Lett. A **145** (1990) 471; Phys. Rev. B **42** (1990) 992.
- [9] Kent A. D., Zhong Y., Bokacheva L., Ruiz D., Hendrickson D. N., and Sarachik M. P., Europhys. Lett. **49** (2000) 521.
- [10] Weiss U., *Quantum Dissipative Systems*, (World Scientific, Singapore, 1993).
- [11] Barra A. L., Gatteschi D., and Sessoli R., Phys. Rev. B **56** (1997) 8192.
- [12] Mirebeau I., Hennion M., Casalta H., Andres H., Gudel H. U., Irodova A. V., and Caneschi A., Phys. Rev. Lett. **83** (1999) 628.
- [13] Stoner E. C. and Wohlfart E. P., Philos. Trans. R. Soc. London, ser. A **240** (1948) 599; reprinted in : IEEE Trans. Magn. **MAG-27** (1991) 3475.

TABLES

TABLE I. Comparison of the splitting (8) with the one from the numerical diagonalization for $S = 10$, $h_x = 0.05$, and $h_z = 0.1$.

m	pert.	diag.
-6	0.156	8.53×10^{-2}
-7	1.01×10^{-3}	7.38×10^{-4}
-8	2.72×10^{-6}	2.26×10^{-6}
-9	3.14×10^{-9}	2.78×10^{-9}
-10	1.40×10^{-12}	1.28×10^{-12}

FIGURES

FIG. 1. m_t/S vs. h_x for a given value of h_z . The range of h_z is $0 \sim 0.9$.

FIG. 2. m_d vs. $\bar{T}(\equiv T/(DS))$ for $h_z = 0.1$, where $h_x = 0.05$ (a), 0.1 (b), and 0.15 (c). Inset: $h_z = 0.4$, where $h_x = 0.04$ (a), 0.06 (b) and 0.1 (c).

FIG. 3. Phase boundary between the first- and the second-order crossover obtained by the quasiclassical (b), the perturbative (c) and the diagonalization method (d). The critical field [13] ($h_{xc}^{2/3} + h_{xc}^{2/3} = 1$) is represented in (a).

FIG. 4. Crossover temperature $\bar{T}_0^{(c)}(\equiv T_0^{(c)}/(DS))$ at the phase boundary between first- and second-order crossover, based on the quasiclassical (a), the perturbative (b) and the diagonalization method (c)

FIG. 5. $\bar{\Gamma}(\equiv \Gamma(T)/\Gamma(0))$ vs. $\bar{T}(\equiv T/(DS))$ for $h_z = 0.1$, where $h_x = 0.05$ (a), 0.1 (b), 0.15 (c), and 0.2 (d). Inset: $h_z = 0.4$, where $h_x = 0.04$ (a), 0.06 (b) and 0.1 (c).









